NASA TECHNICAL NOTE

NASA TN D-6686

c.1

NASA TN D-6686

ULTRAVIOLET RADIATION EFFECTS ON THE INFRARED DAMAGE RATE OF A THERMAL CONTROL COATING

by James A. Bass

Goddard Space Flight Center
Greenbelt, Md. 20771

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • MAY 1972

1. Report No. NASA TN D-6686	2. Government Accession No.
3.	
4. Title and Subtitle: Ultraviolet Radiation Effects on the Infrared Damage Rate of a Thermal Control Coating	5. Report Date: May 1972
	6. Performing Organization Code
7. Author(s): James A. Bass	8. Performing Organization Report No.: G-1055
9. Performing Organization Name and Address: Goddard Space Flight Center, Greenbelt, Maryland 20771	10. Work Unit No.
	11. Contract or Grant No.
12. Sponsoring Agency Name and Address: National Aeronautics and Space Administration, Washington, D.C. 20546	13. Type of Report and Period Covered: Technical Note
	14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The effects of ultraviolet radiation on the infrared reflectance of ZnO-silicone white thermal coatings were investigated. Narrow-band ultraviolet radiation for wavelengths in the 2200Å to 3500Å range was provided by a Bausch and Lomb monochromator and a high pressure, 150-W Eimac xenon lamp. The bandwidth of the monochromator was determined with a Cary Model 14 spectrophotometer. The sample was irradiated while in a vacuum of at least 10^{-6} torr, and infrared reflectance was measured *in situ* with a Beckman spectroreflectometer at 19,500Å.

Reflectance degradation was studied as a function of wavelength, time, intensity, and dose. Damage is wavelength dependent at constant exposure, but no maximum was evident above the shortest wavelength investigated here. The degradation rate at constant intensity is an exponential function of time. It varies with intensity as the sum of terms containing $\sqrt{I}$ and I when the exposure time is constant. However, the degradation cannot be correlated with dose ($I \times t$) because the scatter in the data is too great.

17. Key Words Suggested by Author: Ultraviolet irradiation, Infrared reflectance Thermal control coating, Intensity of irradiation, Duration of irradiation, Wavelength of irradiation	18. Distribution Statement: Unclassified-Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
Unclassified	Unlimited	9	$3.00

*For sale by the National Technical Information Service, Springfield, Virginia 22151

CONTENTS

	Page
Abstract	i
INTRODUCTION	1
APPARATUS	2
TEST PROCEDURE	3
RESULTS AND DISCUSSION	3
CONCLUSIONS	6
References	8
Appendix A – Bandwidth Determination	9

ULTRAVIOLET RADIATION EFFECTS ON THE INFRARED DAMAGE RATE OF A THERMAL CONTROL COATING

by
James A. Bass
Goddard Space Flight Center

INTRODUCTION

The degradation of the infrared reflectance of thermal control coatings by ultraviolet radiation has been previously studied by numerous researchers. The work of Colony* and Greenberg (Reference 1) is typical of the research; they obtained data on thermal-control coatings by the use of the gross spectral characteristics of a mercury light source. However, few simulated degradation experiments using monochromatic light at various intensities from this type of source have been performed on paints, their components, or other thermal-control coatings.

Arvesen (Reference 2) conducted experiments to determine the spectral sensitivity of selected thermal-control coatings: TiO_2/epoxy, ZnO/methyl silicone (S-13), and ZnO/K_2SiO_3 (Z-93). The increase in solar absorptance per energy dose was used to evaluate the sensitivity of a coating to radiation in specific wavelength regions. Irradiations were performed in a vacuum with a high-intensity xenon arc lamp that was selectively filtered with bandpass and short-wavelength cutoff filters. Degradation in each case was found to be quite dependent on the wavelength of the incident radiation, increasing as the wavelength decreased; radiation with wavelengths shorter than 3000Å was observed to be significantly more damaging. The irradiation system allowed different areas of any sample to be exposed simultaneously to different wavelength bands and, therefore, enabled the detection of damage as a function of photon energy.

McCargo *et al.* (Reference 3), experimenting with ZnO/K_2SiO_3 and La_2O_3/K_2SiO_3 as thermal control coatings, observed that more damage resulted from filtered electromagnetic radiation with wavelengths less than 4000Å from a xenon source than from radiation with wavelengths greater than 4000Å. His results qualitatively substantiated those of Arvesen.

Swofford, Mangold, and Johnson (Reference 4) undertook an experimental investigation of the amount of degradation resulting from the irradiation of thermal-control coatings with α (solar absorptance) = 0.25, using radiation in the band from 2000Å to 500Å. Damage incurred by 2000Å to 900Å radiation was of the same order of magnitude as that incurred by 4000Å to 2000Å radiation. Also, coatings exposed to 2000Å to 500Å radiation exhibited more damage than those exposed to 2000Å to 900Å radiation. It remains to be shown,

*Colony, Joe A., "The Preparation and Space Environment Behavior of a Silicate-Treated Zinc Oxide Thermal Control Coating—101", NASA Goddard Space Flight Center Document X-713-70-194, May 1970.

therefore, that radiation in the interval from 900Å to 500Å is especially damaging. These results, however, substantiate the Arvesen investigation; they provide only limited qualitative data, since the energy and wavelength parameters were not carefully controlled or defined. Consequently, any attempts to explain the mechanisms from these data are premature.

Arvesen (Reference 2) further concluded from his experiments that the relative spectral sensitivity of his coatings was virtually independent of intensity and that the effect of total dose (intensity $\times$ time) was constant. Our investigations revealed that the effects of exposure time, intensity, and dose produce independent sets of data.

The effects of ultraviolet radiation of various wavelengths, intensities, and durations on the infrared reflectance of ZnO-silicone coatings were studied to clarify the relative importance of intensity and dose as parameters and to obtain further insight into the nature of reflectance degradation. The coating sample under examination was composed of zinc oxide (New Jersey Zinc Co. SP-500) and methyl silicone resin (General Electric Co. RTV-602), combined with toluene and a tetramethyl ammonium hydroxide catalyst. When this coating was irradiated with ultraviolet light at constant intensity for various intervals of time, the rate of damage was an exponential function of the time. This held true for each new intensity and time interval. When the exposure time was held constant, the damage varied with the intensity of illumination, I, as the sum of terms containing $\sqrt{I}$ and I.

Because of the scatter of the data points, a precise relationship could not be obtained between the damage and the total dose. As indicated before, the effect of total energy dose could not be treated as constant for our data.

APPARATUS

The apparatus used in these experiments consisted of four major components: a vacuum system, a high-intensity monochromator, a spectroreflectometer, and a high-intensity xenon lamp.

The vacuum system included a liquid-nitrogen-cooled sorption pump for roughing, a Varian 8 l/sec Vacion pump that provided working pressures of from 1×10^{-6} to 1×10^{-8} torr, and a radiation cell with a supersil quartz window where the sample was positioned during evacuation, irradiation, and measurement. The sample was aligned perpendicular to the beam, flat against the inside surface of the window.

Radiation with any wavelength from 7000Å to 2000Å could be selected with the high-intensity Bausch and Lomb monochromator. The entrance and exit slits were adjusted to provide a large enough area for measurement of resultant damage at the sample position.

A Beckman DK-2A spectroreflectometer, with a range from 24,000Å to 3000Å, was used to measure the spectral reflectance of the sample. When a measurement was desired, the entire vacuum system was moved to place the quartz window flat against the integrating sphere port.

The source of irradiation was a high-pressure, 150-W, Eimac xenon lamp with an internal rhodium reflector. It was ideal for these experiments because of its high output of short wavelength radiation. This was delivered, within 3 deg of the beam axis, on the monochromator input slit. Thus, high-intensity, narrow-band radiation could be focused on the sample over an area sufficient for reflectance measurements.

TEST PROCEDURE

The absolute energy distribution and bandwidth of the radiation from the monochromator (Appendix A) were determined by use of a Cary Model 14 spectrophotometer which utilized a standard tungsten lamp.

Intensity measurements were made at the sample position with a special flat-response, high-sensitivity, Epply thermopile. Although the maximum intensity was detected at 2600Å with the monochromator and thermopile, the absolute measurement revealed that the wavelength of maximum intensity actually occurred at 2500Å, with lesser peaks located at 2685Å and 2350Å.

By using the planimeter, 97 percent of the radiation beam was calculated to be within a ±200Å band-with of 2600Å.

The sample was attached to a sample holder and the cell was evacuated to at least 10^{-6} torr with the aid of the liquid-nitrogen-cooled sorption pump. After the infrared reflectance of the sample was measured (Figure 1), it was exposed (Figure 2) to the desired ultraviolet radiation at the selected intensity for a predetermined amount of time before the reflectance was measured again. The wavelength of 19,500Å was chosen for data compilation because maximum sensitivity to damage was observed there. All reflectance measurements were *in situ*; that is, the vacuum environment was retained while the various measurements were performed.

RESULTS AND DISCUSSION

The damage dependent on the wavelength, as shown in Figure 3. Degradation increased from 3500Å to 2200Å. The curve indicates that most of the damage due to the radiation occurs considerably below the edge of the ultraviolet-radiation band (3800Å). Unfortunately, insufficient energy at shorter wavelengths prohibited the extension of this investigation, and a maximum damaging wavelength, such as the one reported by Donohoe (Reference 5) for anodized aluminum, has not yet been detected.

Time and intensity relationships were investigated in the bandpass 2600Å ± 200Å because considerable damage occurred there, and also because a wide range of intensities was available. The damage increased as a function of time, as shown in Figure 4 for three constant intensities of radiation. In each case, the damage is an exponential function of time, and the optical effect, damage per unit time, steadily decreases. Over the limited time range considered here, these curves can be described by the relationship

$$\Delta r(I,t) = \Delta r_1(I)(1-e^{-t/\tau}), \tag{1}$$

where

Δr = change in reflectance

and

$$\Delta r_1(I) = K_1\sqrt{I} + K_2 I.$$

Figure 4 also shows points calculated from this relationship with $\tau = 0.55$ hours so that they may be compared with laboratory data.

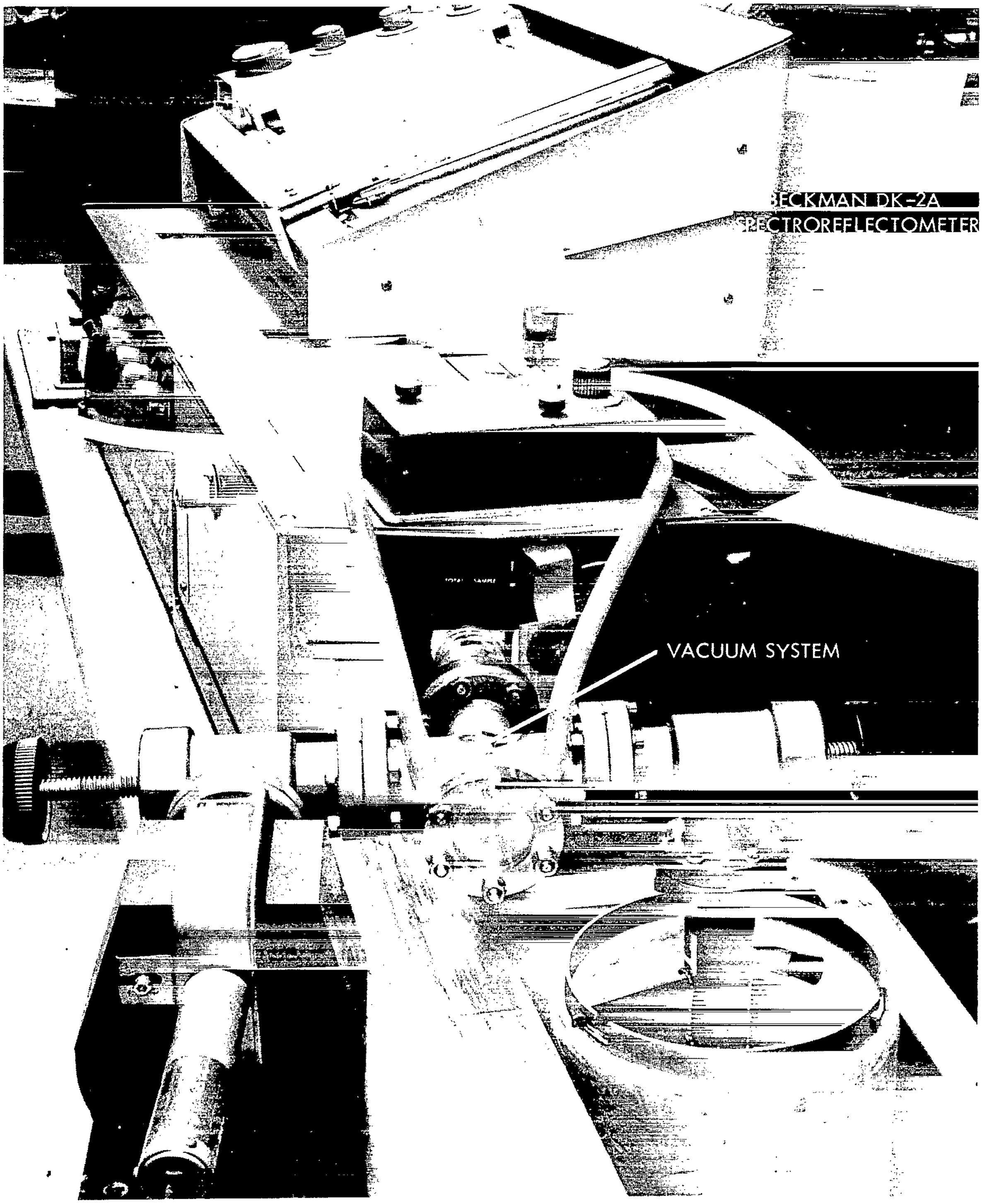


Figure 1—Apparatus for measurement of spectral reflectance of samples.

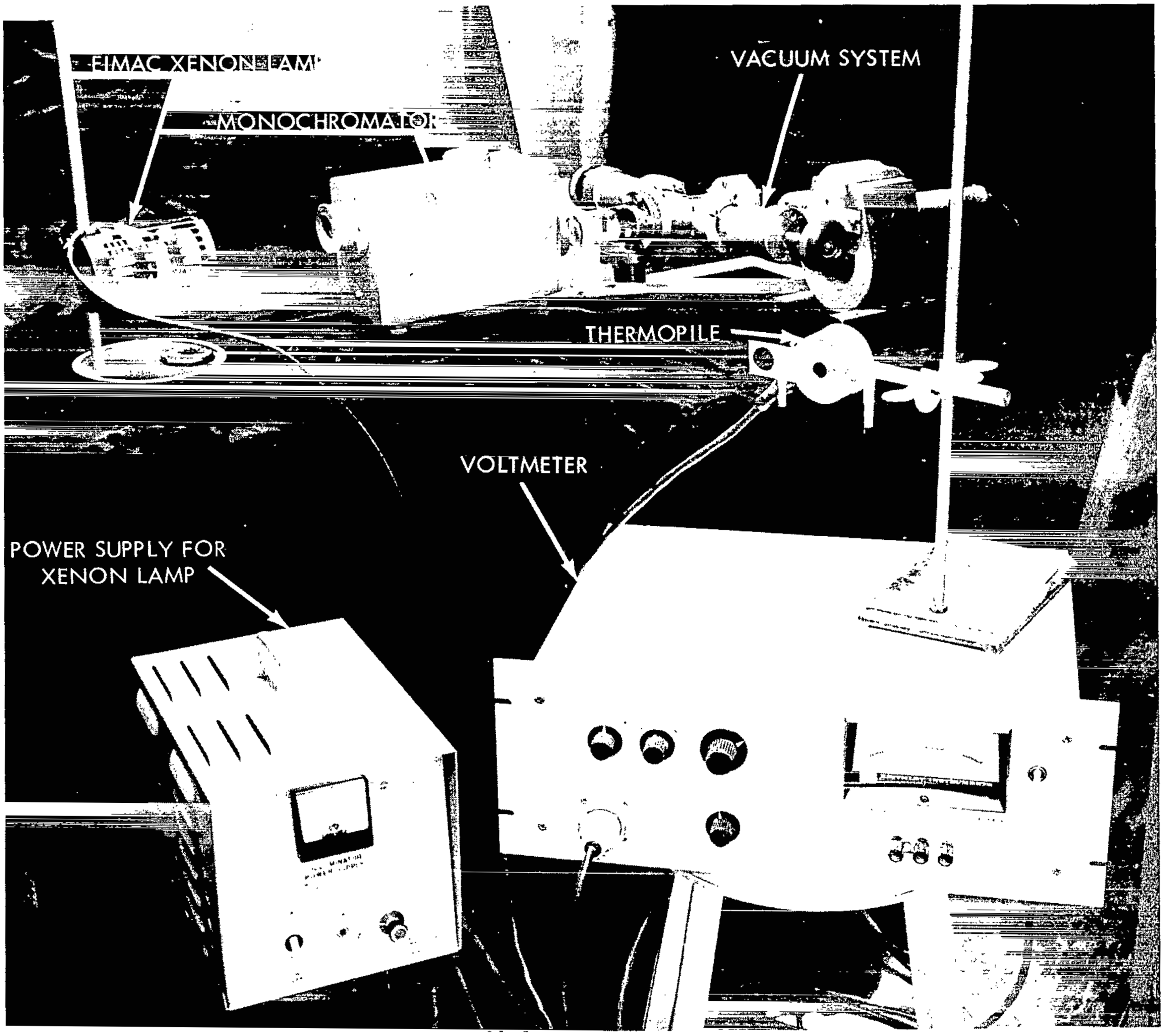


Figure 2—Apparatus for ultraviolet irradiation of samples.

When the data were replotted, with damage expressed as a function of intensity and with the time of exposure held constant, another simple relationship was observed (see Figure 5). Specifically, the change in reflectance at 19,500Å was seen to be proportional to the square root of the intensity after 4 hours of exposure:

$$\Delta r_2(I) = K_1 \sqrt{I}, \tag{2}$$

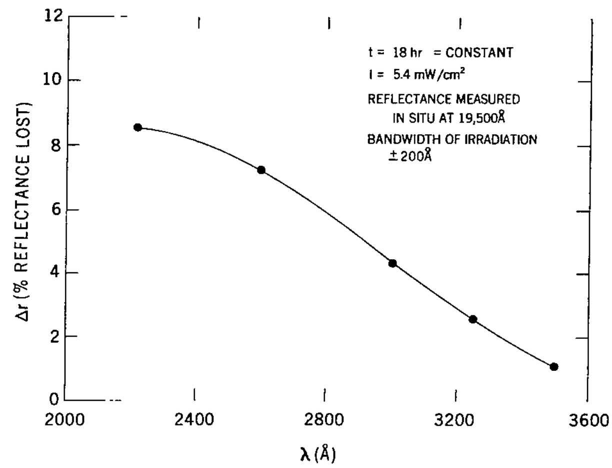


Figure 3—Wavelength dependence of infrared reflectance damage at constant dose, 97 (mW-hr)/cm^2.

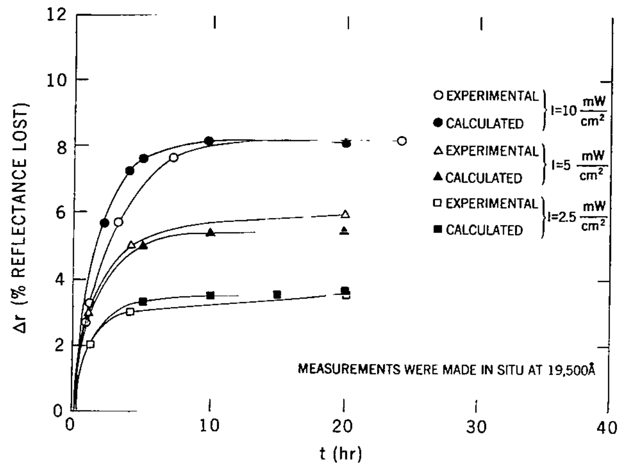


Figure 4—Time dependence of infrared reflectance damage, $\lambda = 2600$Å.

with $K_1 = 2.00\ (\mathrm{mW/cm^2})^{-1/2}$. When the coating had been exposed for 20 hours, however, the degradation could be viewed as the sum of the four-hour curve and a term proportional to I, so that now

$$\Delta r_1(I) = K_1 \sqrt{I} + K_2 I, \tag{3}$$

where $K_2 = 0.185\ (\mathrm{mW/cm^2})^{-1}$. Overall, the data indicate the relationship

$$\Delta r(I,t) = (K_1 \sqrt{I} + K_2 I)(1 - e^{-t/\tau}). \tag{4}$$

Figure 5 also shows points calculated with the specified constants for all curves.

A possible explanation for this behavior is that, after four hours of exposure, another process became evident. The first-power intensity function may be attributed to the binder, and the square-root intensity function may be attributed to electron-hole generation in ZnO (Reference 6).

The change in reflectance was plotted as a function of total dose ($I \times t$) (Figure 6). From the scatter of the data points, it is apparent that no simple relationship exists.

CONCLUSIONS

The results of an experimental investigation indicate that the rate of damage by ultraviolet radiation to a ZnO-silicone coating is a function of wavelength, intensity, dose, and time. The degradation rate increased as incident radiation wavelength decreased from 3500Å to 2200Å. It was also observed that this rate is proportional to the square root of the illumination intensity for 4 hours of irradiation and to the sum of square root and first power terms for 20 hours of exposure. When damage was plotted as a function of time for constant intensities, an exponential function was obtained. It was also shown that the effect of total dose should not be considered constant, as many investigators have assumed. Instead, it is affected independently by intensity and time.

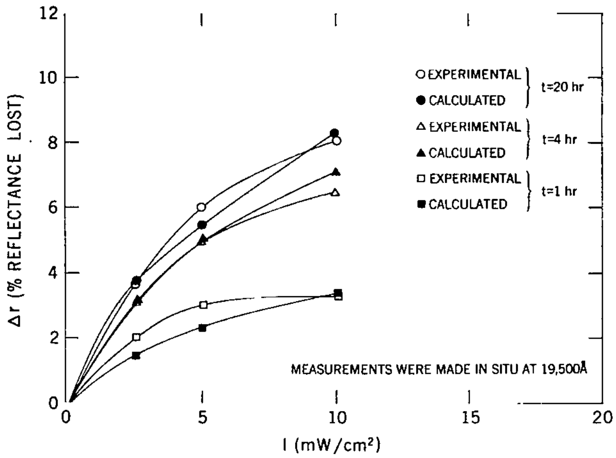


Figure 5—Intensity dependence of infrared reflectance damage, $\lambda = 2600$Å.

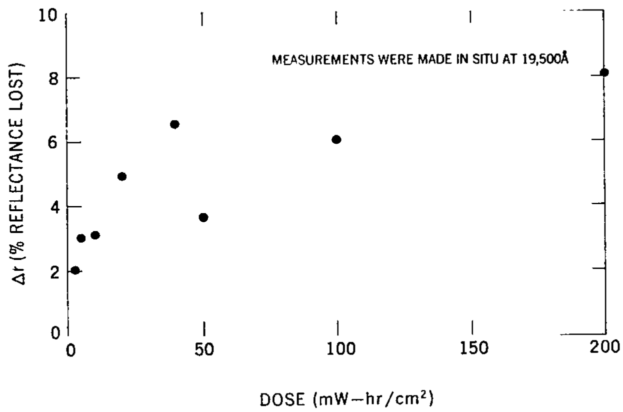


Figure 6—Absence of simple relationship between degradation rate and dose, $\lambda = 2600$Å.

ACKNOWLEDGMENTS

The author is extremely grateful for the assistance, encouragement, and continued interest of Joe A. Colony, Dr. John B. Schutt, and James D. Mann in the preparation of this document.

Goddard Space Flight Center
National Aeronautics and Space Administration
Greenbelt, Maryland, December 4, 1970
124-09-26-15-51

REFERENCES

1. Greenberg, S. A., "Solar Radiation Induced Damage to Optical Properties of ZnO-Type Pigments," NASA Contractor Report 61429, National Aeronautics and Space Administration, Washington, D.C., 1968.

2. Arvesen, John C., "Spectral Dependence of Ultraviolet Induced Degradation of Coatings for Spacecraft Thermal Control," Paper No. 67-340, AIAA Thermophysics Specialist Conference, New Orleans, La., April 17-20, 1967.

3. McCargo, M., Greenberg, S. A., and Douglas, N. J., "Radiation-Induced Absorption Band in Spacecraft Thermal Control Coating Pigments," Paper No. 69-642, AIAA 4th Thermophysics Conference, San Francisco, California, June 16-18, 1969.

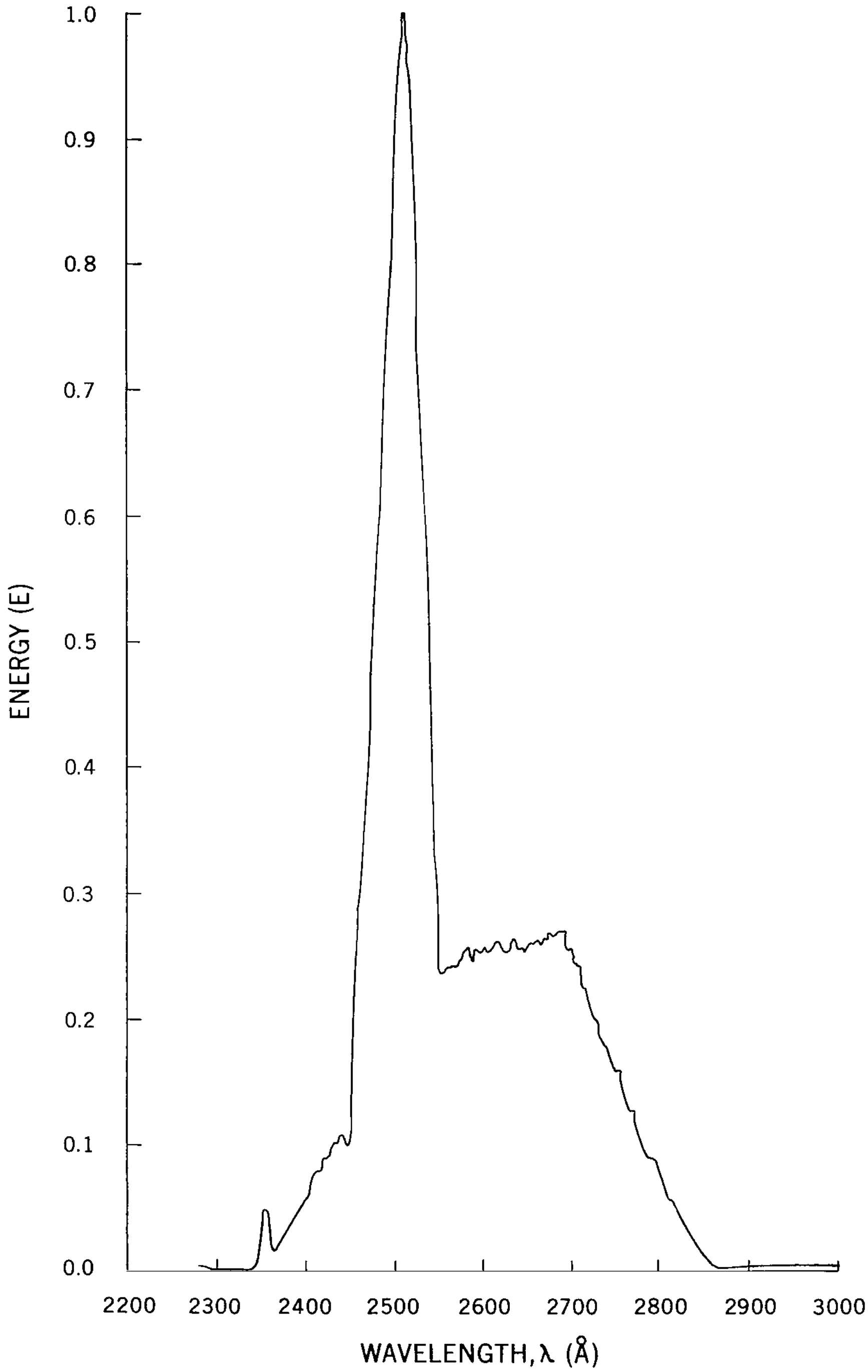
4. Swofford, D. D., Mangold, V. L., and Johnson, S. W., "The Effects of Extreme Ultraviolet on the Optical Properties of Thermal Control Coatings," Paper No. 68-783, AIAA 3rd Thermophysics Conference, Los Angeles, California, June 1968.

5. Donohoe, M. J., Henninger, J. H., and McIntosh, R., "The Degradation of Alzak by Short Wavelength Ultraviolet Radiation," presented at Space Simulation Conference, Gaithersburg, Maryland, September 14, 1970.

6. Morrison, S. R., and Sancier, K. M., "The Effect of Environment on Thermal Control Coatings," NASA Contractor Report 100210, National Aeronautics and Space Administration, Washington, D.C., 1969.

Appendix A

Bandwidth Determination



NASA-Langley, 1972 —— 18

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546

OFFICIAL BUSINESS
PENALTY FOR PRIVATE USE $300

FIRST CLASS MAIL

POSTAGE AND FEES PAID
NATIONAL AERONAUTICS AND
SPACE ADMINISTRATION

U.S.MAIL

018 001 C1 U 18 720505 S00903DS
DEPT OF THE AIR FORCE
AF WEAPONS LAB (AFSC)
TECH LIBRARY/WLOL/
ATTN: E LOU BOWMAN, CHIEF
KIRTLAND AFB NM 87117

POSTMASTER: If Undeliverable (Section 158 Postal Manual) Do Not Return

---

"The aeronautical and space activities of the United States shall be conducted so as to contribute . . . to the expansion of human knowledge of phenomena in the atmosphere and space. The Administration shall provide for the widest practicable and appropriate dissemination of information concerning its activities and the results thereof."

—NATIONAL AERONAUTICS AND SPACE ACT OF 1958

NASA SCIENTIFIC AND TECHNICAL PUBLICATIONS

TECHNICAL REPORTS: Scientific and technical information considered important, complete, and a lasting contribution to existing knowledge.

TECHNICAL NOTES: Information less broad in scope but nevertheless of importance as a contribution to existing knowledge.

TECHNICAL MEMORANDUMS: Information receiving limited distribution because of preliminary data, security classification, or other reasons.

CONTRACTOR REPORTS: Scientific and technical information generated under a NASA contract or grant and considered an important contribution to existing knowledge.

TECHNICAL TRANSLATIONS: Information published in a foreign language considered to merit NASA distribution in English.

SPECIAL PUBLICATIONS: Information derived from or of value to NASA activities. Publications include conference proceedings, monographs, data compilations, handbooks, sourcebooks, and special bibliographies.

TECHNOLOGY UTILIZATION PUBLICATIONS: Information on technology used by NASA that may be of particular interest in commercial and other non-aerospace applications. Publications include Tech Briefs, Technology Utilization Reports and Technology Surveys.

Details on the availability of these publications may be obtained from:

SCIENTIFIC AND TECHNICAL INFORMATION OFFICE

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

Washington, D.C. 20546